

# Design and Synthesis of Advanced High-Energy Cathode Materials

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Project ID: ES225

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# Overview

## Timeline

- Start date: October 2016
- End date: September 2019
- Percent complete: 10%

## Budget

- Total project funding
  - FY2016           \$550K
  - FY2017           \$550K

## Barriers Addressed

- Energy density
- Cycle life
- Safety

## Partners

- Interactions/collaborations:  
LBNL, UCB, ANL, Cambridge,  
ORNL, PNNL, NCEM, ALS, SSRL
- Project lead: Vincent Battaglia

# Relevance/Objectives

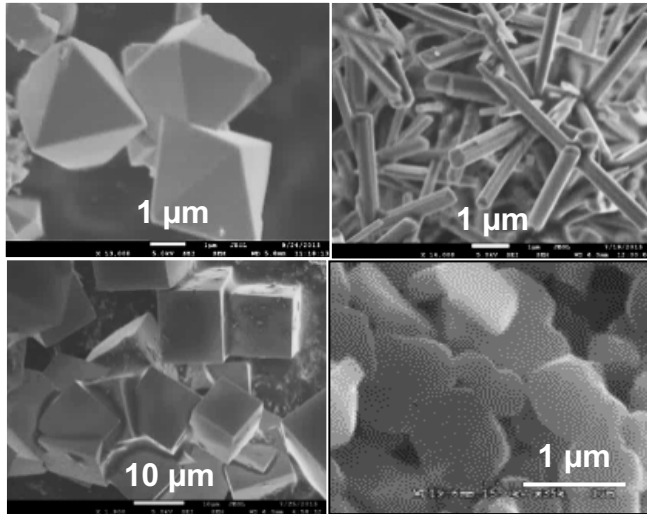
- Obtain fundamental understanding on performance-limiting properties, phase transition mechanisms, kinetic barriers, and instabilities in high-energy cathode materials.
- Develop strategies to improve solid-state charge transport and optimize charge transfer at electrode-electrolyte interface.
- Discover and develop next-generation electrode materials based on rational design as opposed to the conventional empirical approaches.

# Milestones

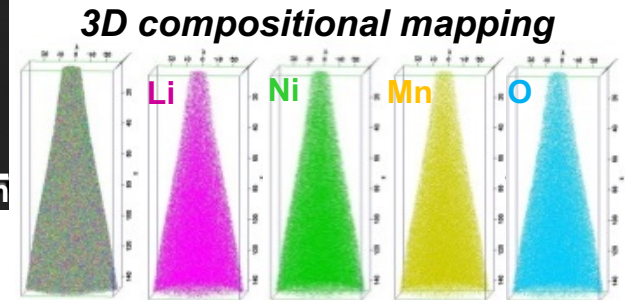
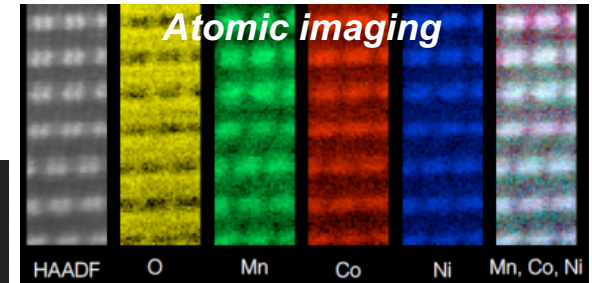
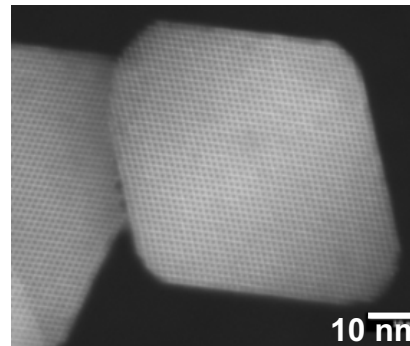
Date	Milestones and Go/No-Go Decision	Status
December 2016	<u>Milestone</u> Synthesize model Li-TM oxide cathode materials with several different chemical compositions and/or morphologies.	Completed
March 2017	<u>Milestone</u> Investigate the bulk activities of TM and O redox centers in Li-TM oxides as a function of SOC and temperature.	Completed
June 2017	<u>Go/No-Go Decision</u> Investigate synthesis methods for preparing single crystals of Li-excess TM oxides with reversible O redox activities. No-Go if high-quality crystals of the oxide cannot be made.	On schedule
September 2017	<u>Milestone</u> Determine the activities of lattice oxygen and TM on particle surface and the impact of cathode chemistry and surface facet on these activities.	On schedule

# Approach/Strategy

Well-formed crystals free of the complexities in conventional samples



Fundamental understanding of solid-state chemistry, kinetic barriers and instabilities during battery operation



**Model-system construction**

**Advanced diagnostics**

**Rational design, synthesis and testing of materials**

**Fundamental knowledge**

# Technical Accomplishments: Overview

I. Obtained new insights on the activities of oxygen sublattice in novel high-capacity Li-excess oxide cathodes

- Synthesized  $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$  cathode with a RT discharge capacity of more than 250 mAh/g.
- Demonstrated Li extraction mechanisms associated with TM oxidation involving the entire particle at low SOC, combined  $\text{O}^{2-}$  oxidation to  $\text{O}^-$  and  $\text{O}_2$  release at high SOC.

II. Evaluated surface engineering approaches to promote stable high-voltage cycling of Li-TM oxide cathodes

- Particle morphology control through synthesis
- Particle size engineering and surface coating

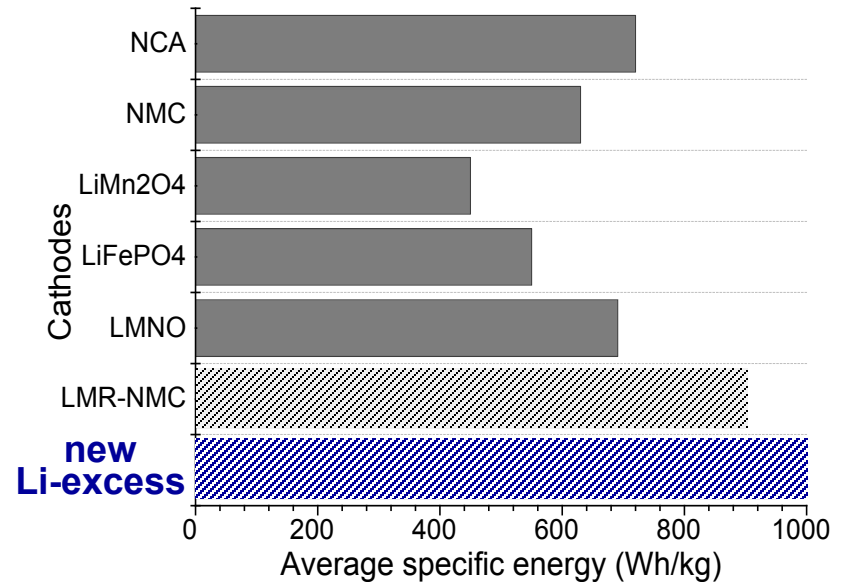
III. Obtained key understanding of phase transformation mechanism and kinetic barriers in intercalation cathodes. Results summarized and published in *Nature Communications*, 8, 14309 (2017).

This presentation focuses on 1) and 2) only.

# I. High-Capacity Li-Excess Oxide Cathodes

- **Why are they interesting**

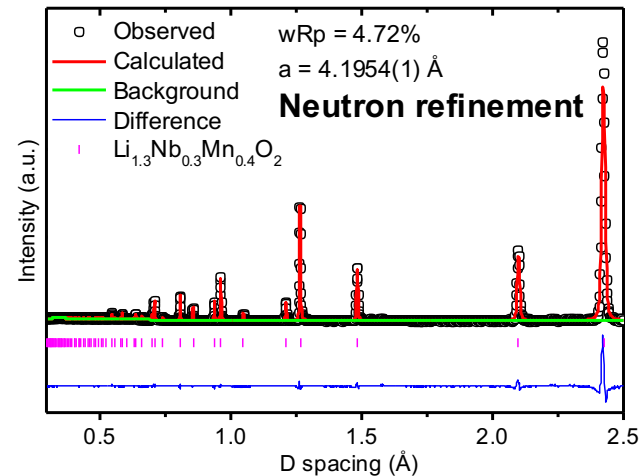
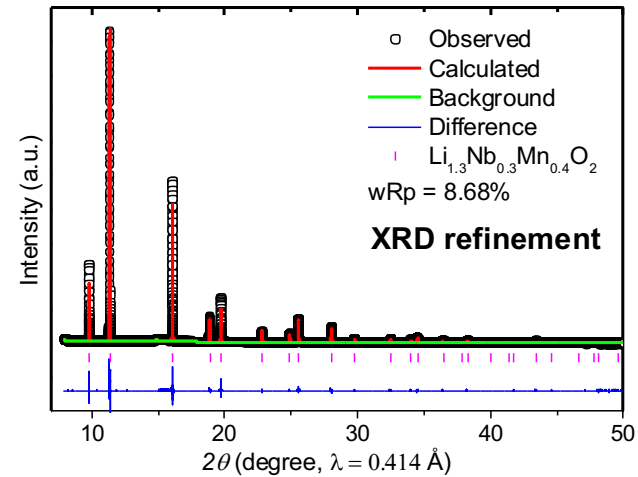
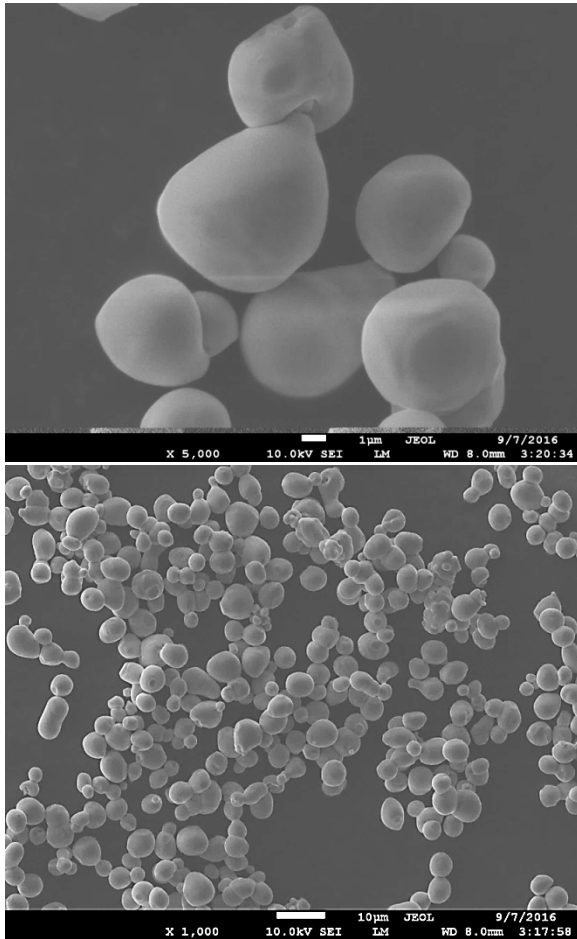
- Li-excess ( $\text{Li}/\text{TM} > 1$ ) cathode materials can utilize more than 1  $\text{Li}^+$  per formula unit to deliver high energy reaching 1000 Wh/kg.
- Possible new battery research direction with a variety of novel chemistry options available.



- **What are the challenges**

- Fundamental understanding of charge storage mechanism in Li-excess oxides lacking: where does the extra capacity come from and how reversible?
- What is the impact of having both cation and anion redox activities on key cathode properties such as kinetics and stabilities (including structural, cycling and thermal)?
- Can structure, morphology and surface modifications improve the performance and enable the use of Li-excess TM oxides as high-energy cathodes?
- $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$  ( $\text{L}_{1.3}\text{NM34}$ ) was selected for this study as it has only one redox active TM (i.e. Mn).

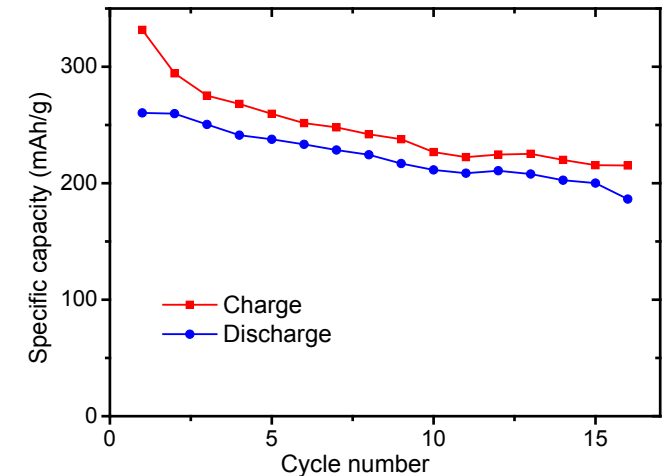
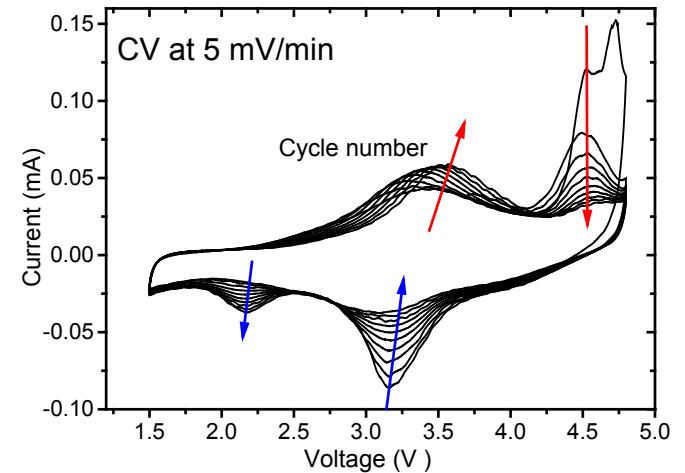
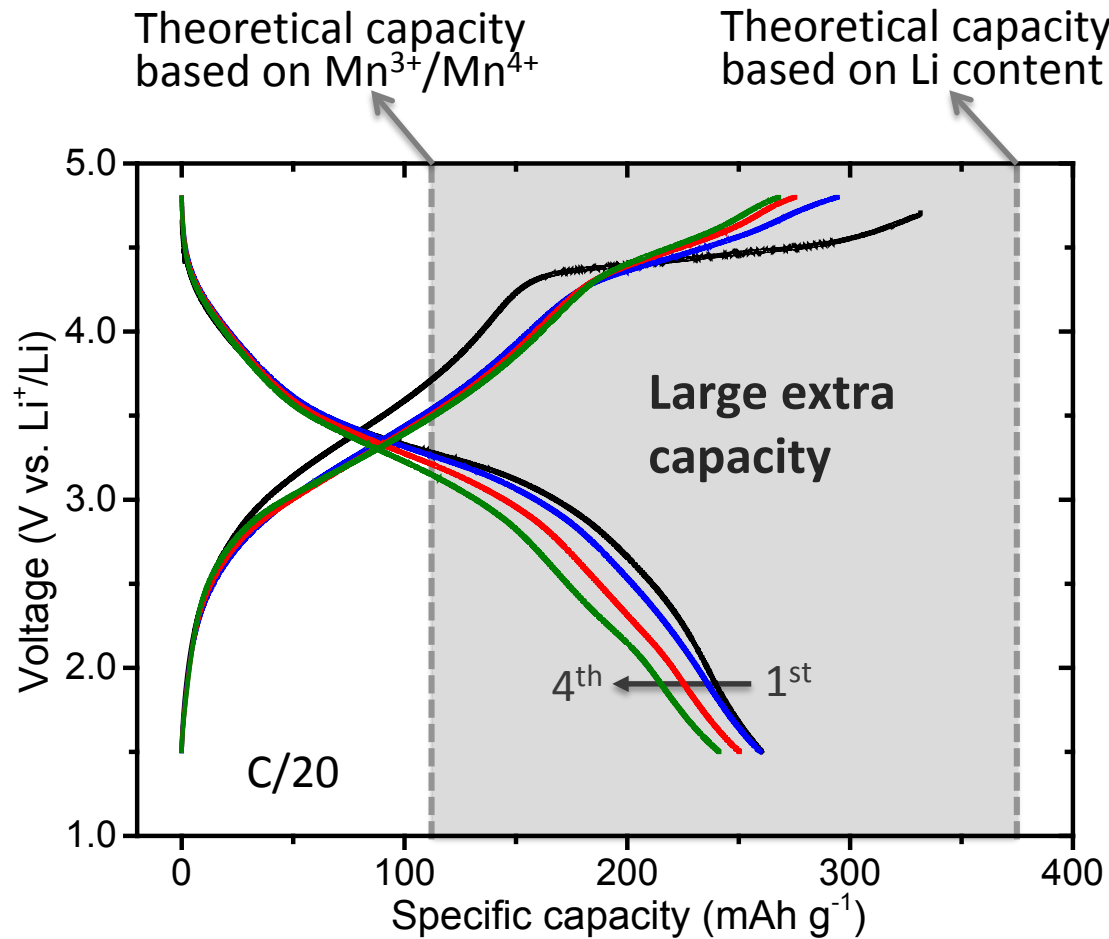
# Synthesis of $\text{Li}_{1.3}\text{NM34}$ crystals



- High-quality  $\text{Li}_{1.3}\text{NM34}$  crystals ( $\sim 5 \mu\text{m}$  in size) synthesized at  $950^\circ\text{C}$  in a KCl flux.
- Refined oxygen occupancy was 0.99(1) – no oxygen vacancy in the pristine material.



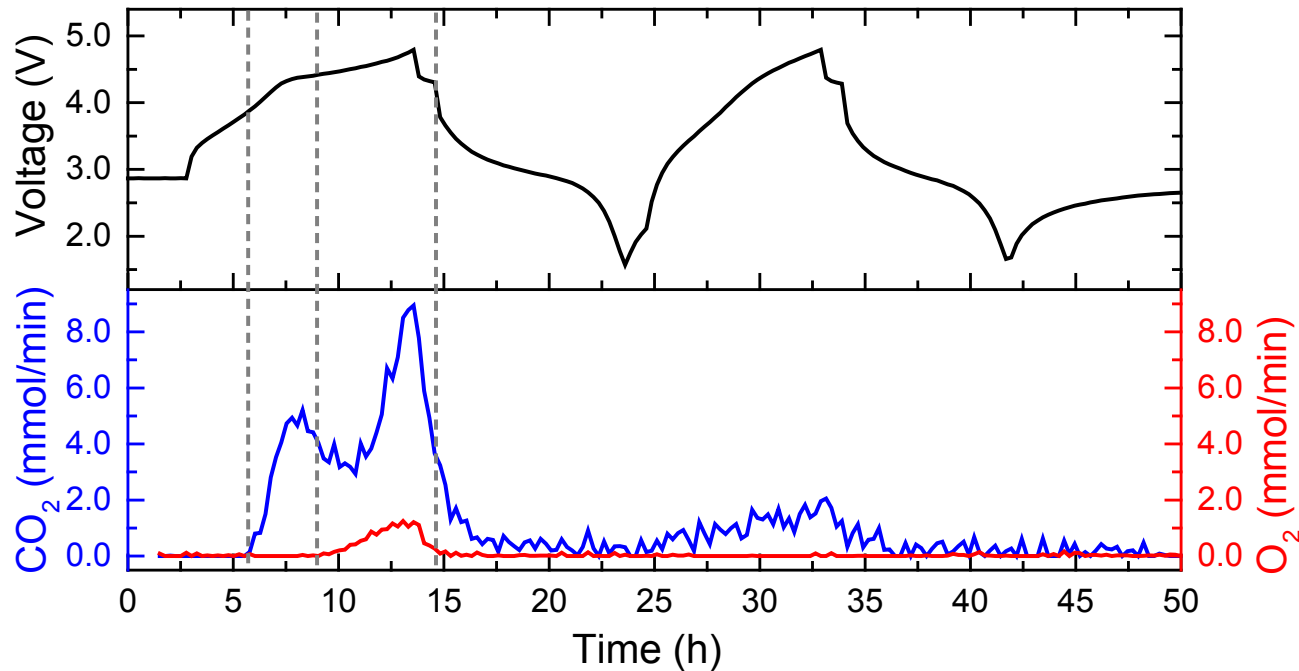
# Electrochemical performance of $\text{Li}_{1.3}\text{NM34}$ at RT



- About 120 mAh/g from Mn redox of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  (0.4  $\text{Li}^+$ ). Source of additional capacity (about 140 mAh/g) unclear.
- First cycle activation plateau becomes slopy but remains in the following cycles – some irreversibility.
- Gradual peak shift towards lower voltage along cycling, similar to voltage fade in LMR.

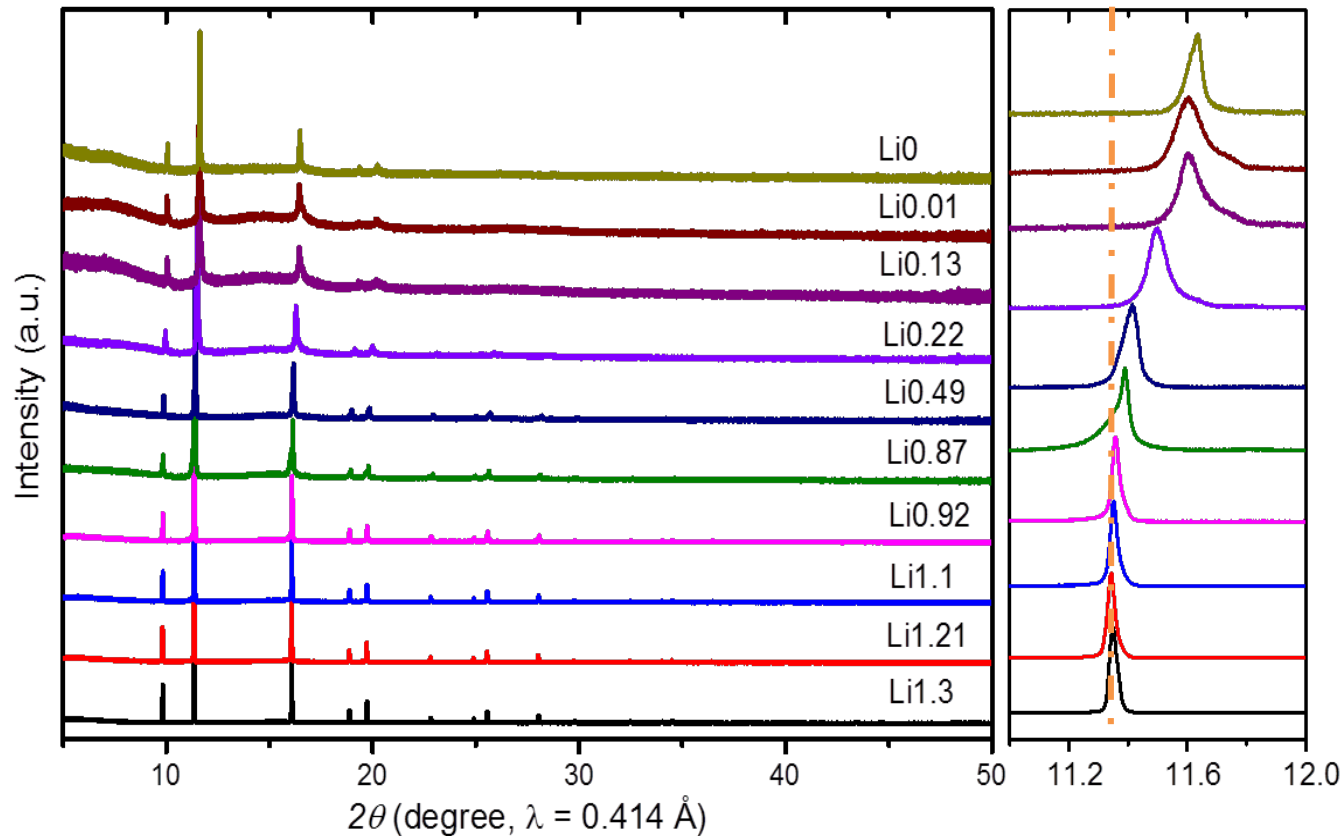
# Gas evolution during $\text{Li}_{1.3}\text{NM34}$ cycling

*Operando DEMS (in collaboration with Bryan McCloskey, UC Berkeley)*



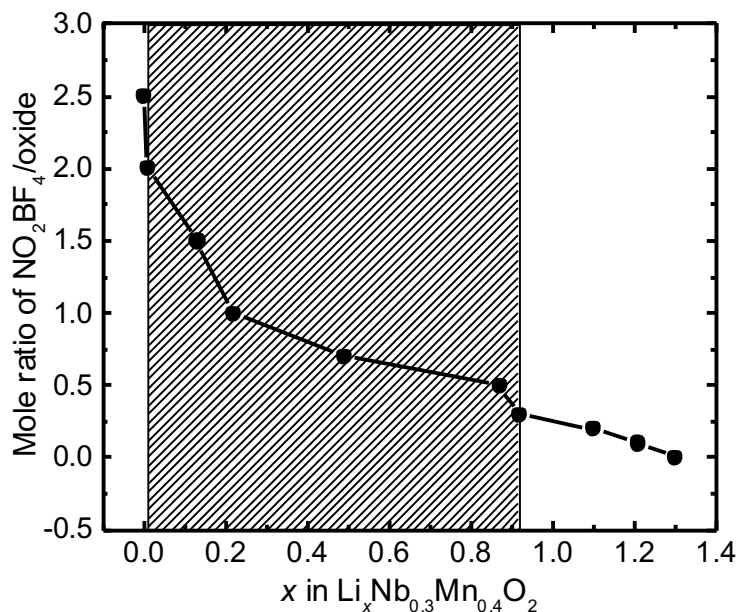
- Oxygen evolution begins near the onset of the first delithiation plateau but negligible  $\text{O}_2$  evolution in the following cycle.
- Significant  $\text{CO}_2$  evolution upon first charge and reduced amount in the following cycle. Electrolyte oxidation involved.

# First delithiation – changes in crystal structure

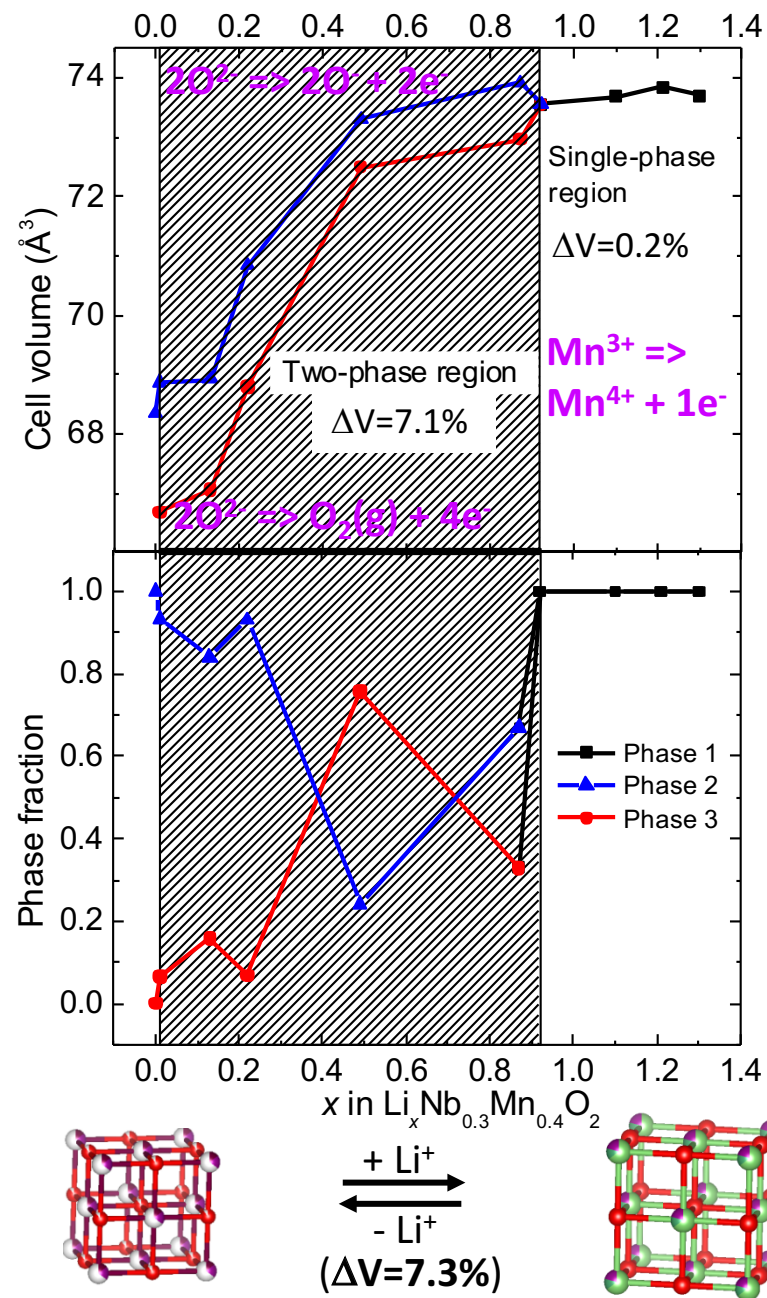


- Delithiated  $\text{Li}_x\text{NM34}$  ( $0 \leq x < 1.3$ ) samples prepared by chemical oxidation with  $\text{NO}_2\text{BF}_4$  in acetonitrile.
- Only rock-salt phases (Fm-3m) observed in the entire Li content range.
- Peak broadening observed below  $\text{Li0.9}$  – short range ordering and smaller domain size upon deep Li extraction.

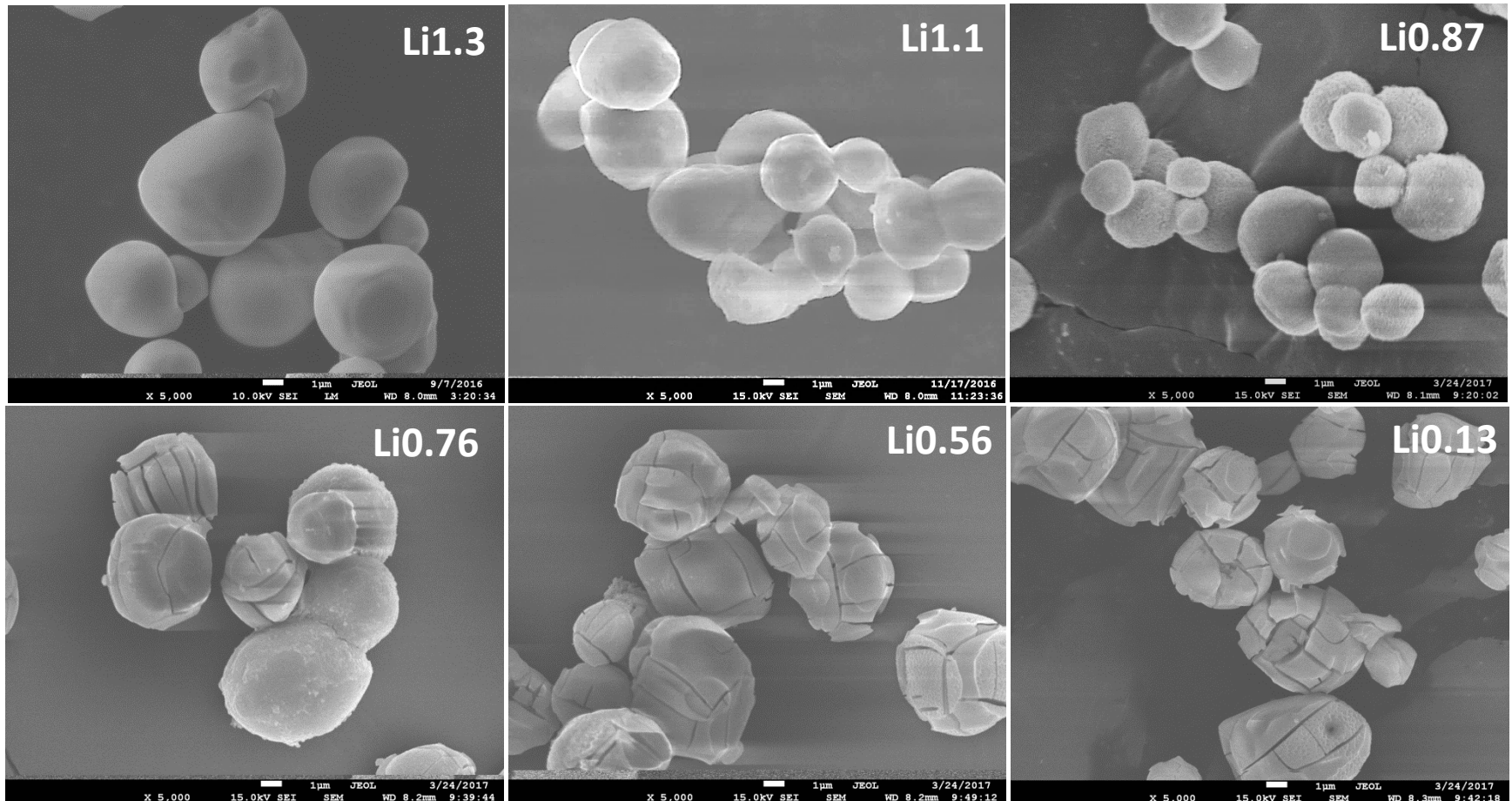
# First delithiation – changes in crystal structure



- Deviation from linear Li extraction kinetics below Li0.9.
- **Above Li0.9** – follows Vegard's law with single rock-salt phase transition involving  $\text{Mn}^{3+}/\text{Mn}^{4+}$  redox and 0.4  $\text{Li}^+$  extraction.
- **Below Li0.9** – evolution of two rock-salt phases with different lattice dimensions, involving complex mixed anion activities.
- Joint XRD and neutron refinement shows oxygen occupancy of 0.92(1) or 8% of oxide ion vacancy in fully delithiated sample – evidence for oxygen loss in the structure.

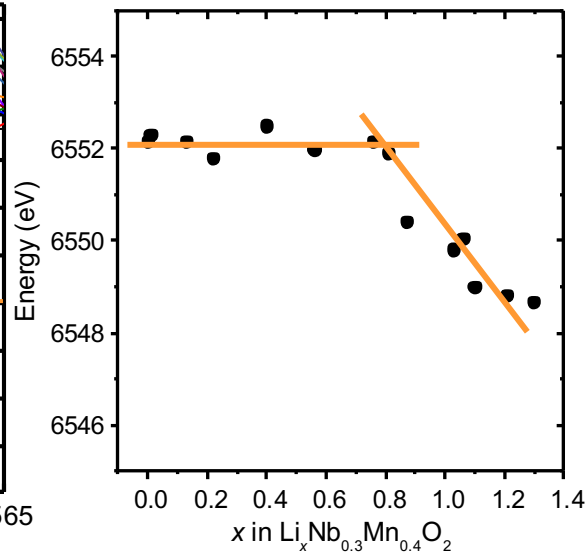
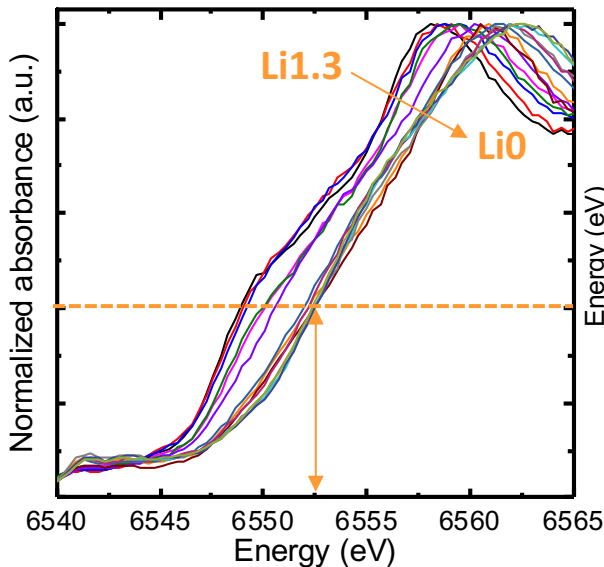
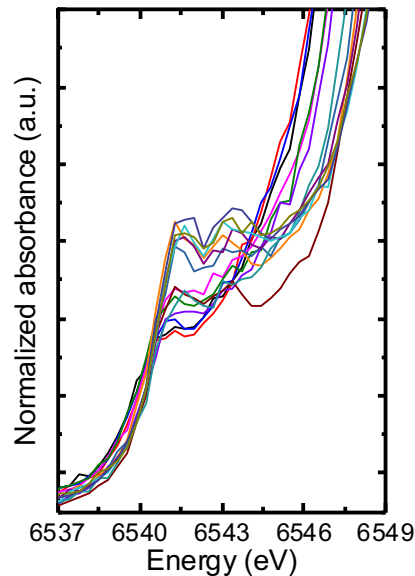
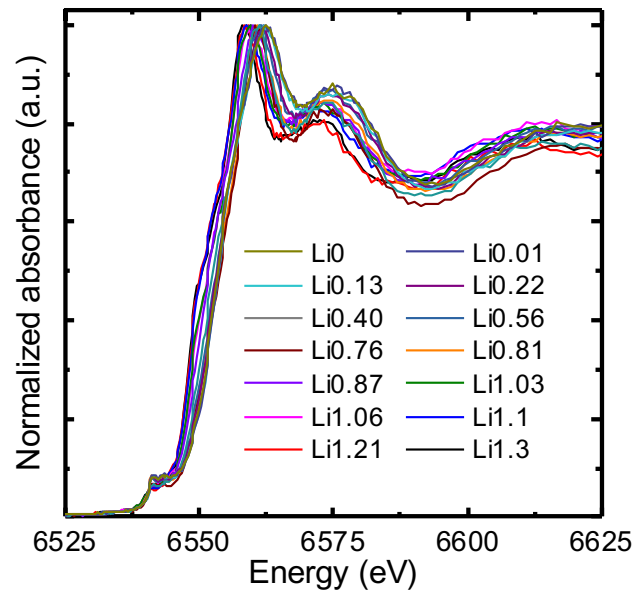


# First delithiation – changes in morphology



- No morphology changes above Li0.9.
- Morphology damage below Li0.9, increasing fracture till ~Li0.56 – combined effects of volume change and oxygen release during delithiation.
- Particle cracking creates new surface and contributes to increased  $O_2$  evolution – surface oxygen stabilization needs to consider morphology evolution during cycling.

# First delithiation – changes in bulk chemical state



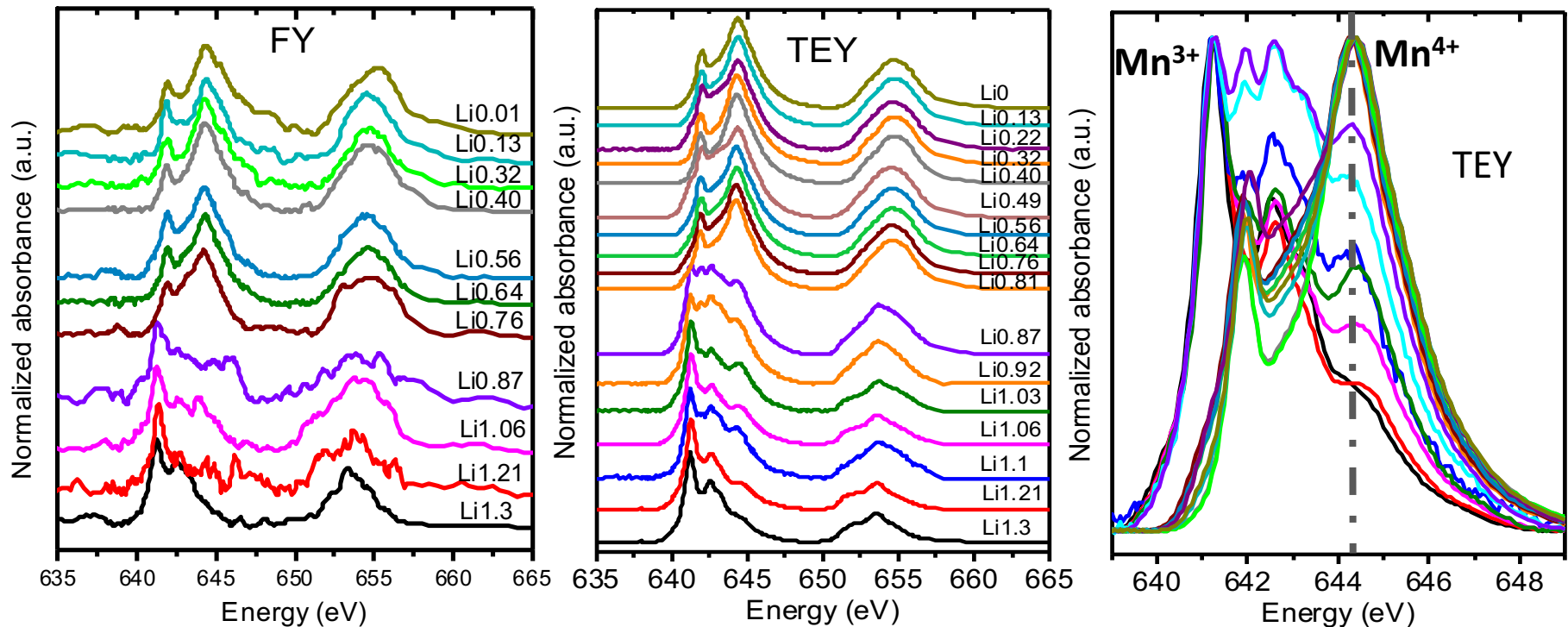
*Mn K-edge hard XAS measurements (SSRL beamline 10-1)*

- Changes in pre-edge peak intensity (or Mn local environment) are segregated in two regions of Li content above and below 0.9.
- Mn K-edge energy shifts to higher value in a near linear fashion above  $\sim \text{Li}0.9$  but no changes observed below  $\sim \text{Li}0.9$  – Mn redox only occurs in  $0.9 < x < 1.3$  region.



# First delithiation – surface vs. bulk chemical state

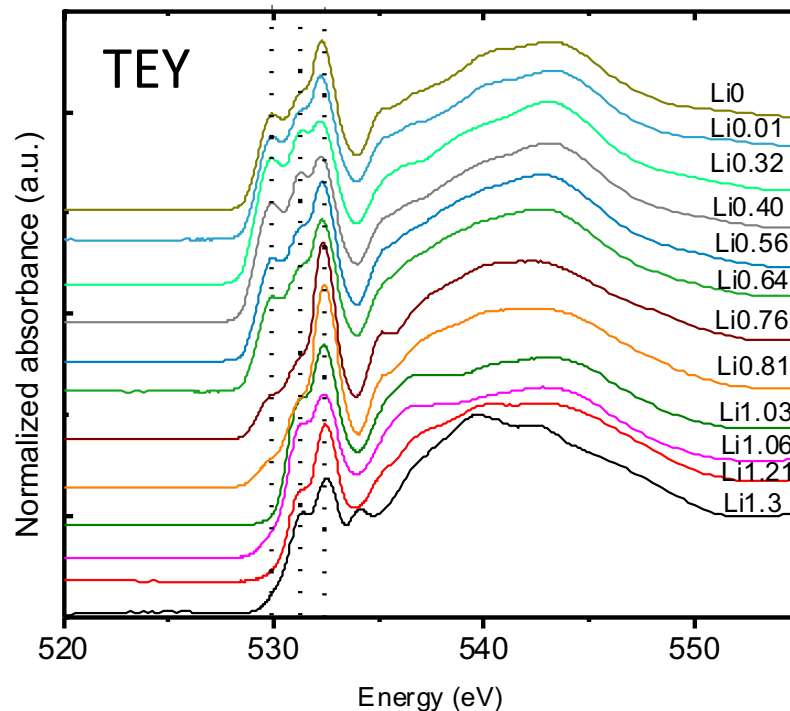
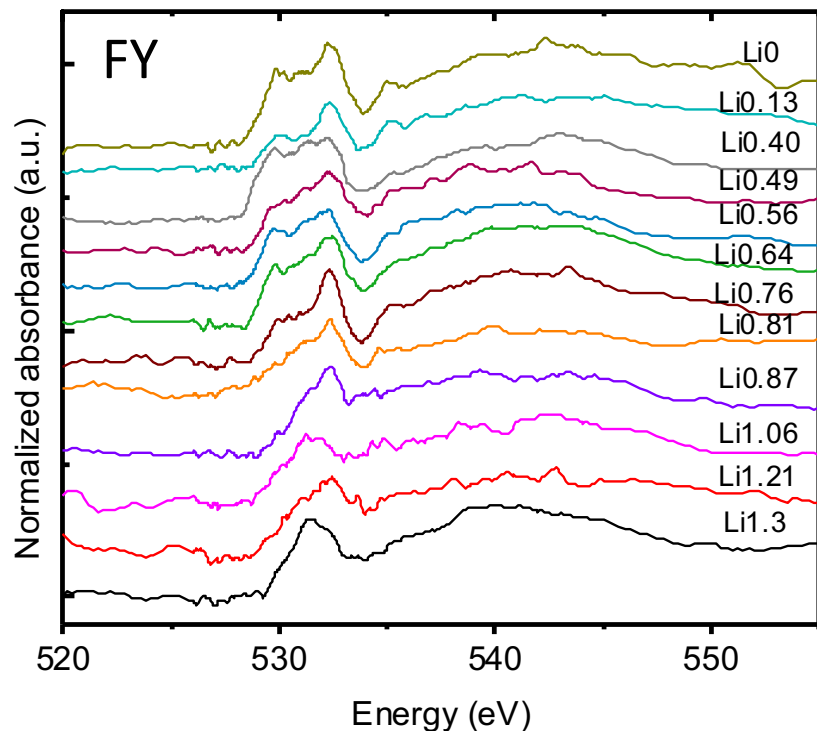
*TEY and FY Mn L-edge soft XAS measurements (SSRL beamline 8-2)*



- TEY probes roughly 5 nm on the surface while FY probes about 50 nm into the bulk.
- Gradual oxidation of Mn<sup>3+</sup> to Mn<sup>4+</sup> above Li0.9 while maintaining Mn<sup>4+</sup> below Li0.9.
- Similar trend in surface and bulk Mn oxidation state changes – Mn redox involves the entire particle uniformly in 0.9 < x < 1.3.

# First delithiation – surface vs. bulk chemical state

*TEY and FY O K-edge soft XAS measurements (SSRL beamline 8-2)*



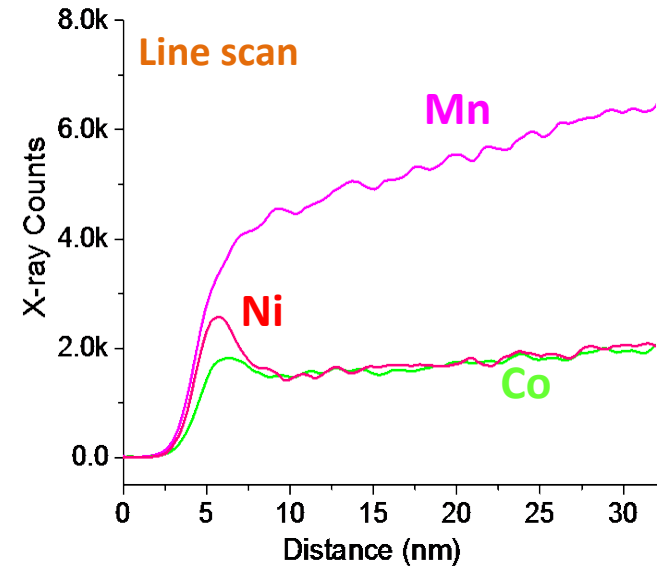
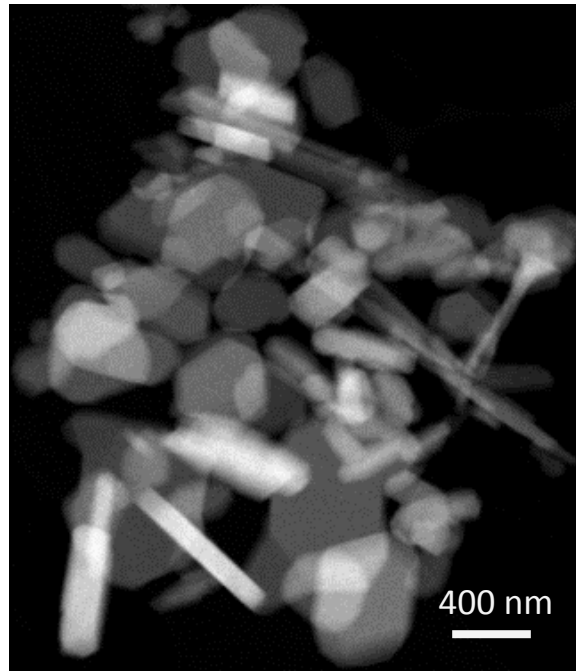
- Significant changes in O K-edge spectra begin around Li0.9 for both surface and bulk.
- Below Li0.9, peak area increases along with the decrease of Li content – participation of O redox.
- Difference observed on TEY and FY O profiles suggest oxygen activity changes from surface to bulk – consistent with  $O^{2-}$  oxidation to  $O^-$  in the bulk and  $O_2$  on the surface.



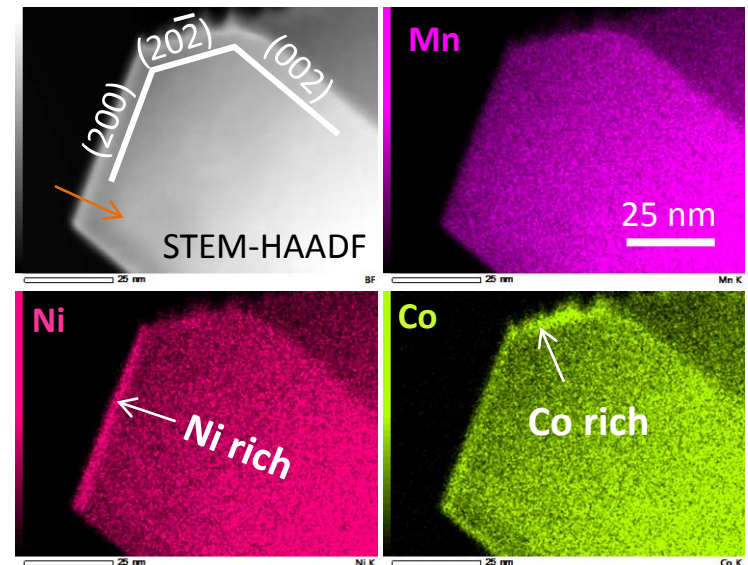
## II. Surface Engineering for Stable Cycling

LMR-NMC141 platelet crystals  
( $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ )

*HAADF STEM  
imaging and XEDS  
mapping (in  
collaboration with  
Chongmin Wang,  
PNNL)*

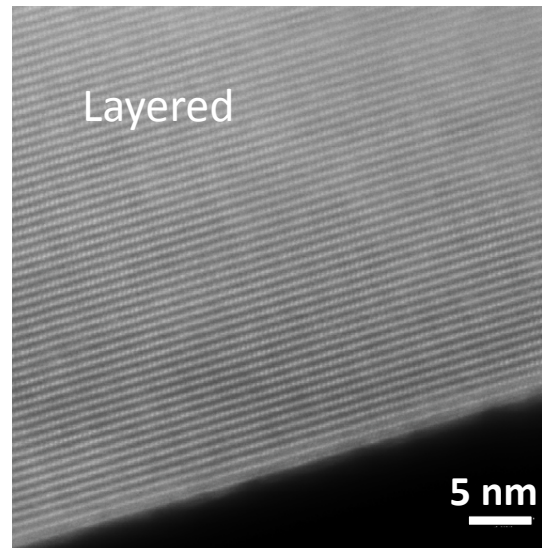
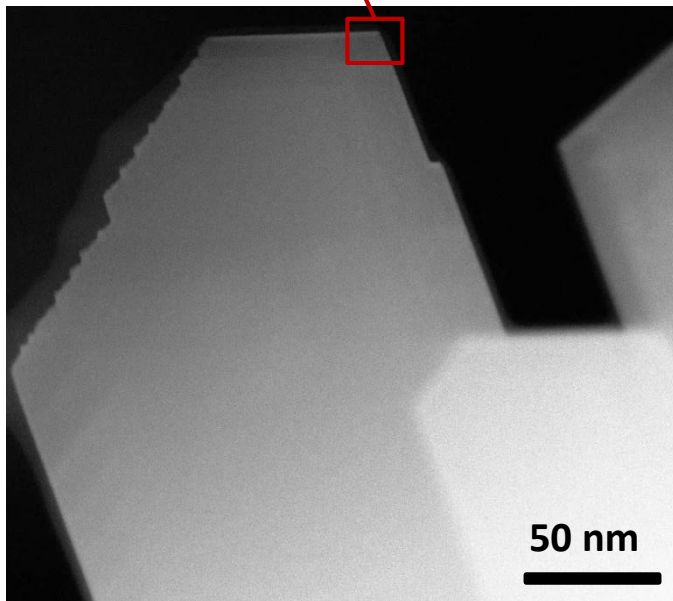
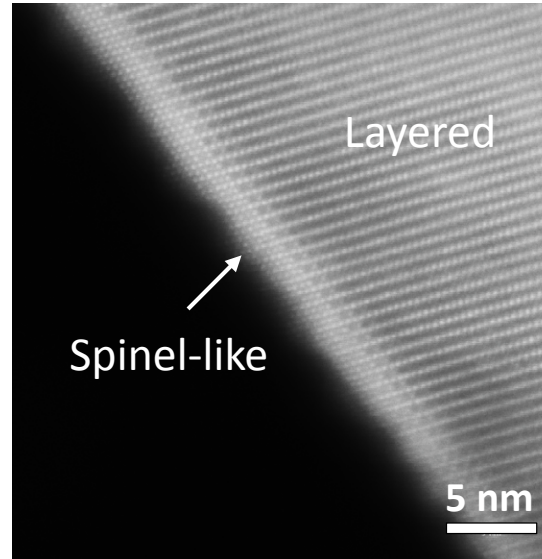
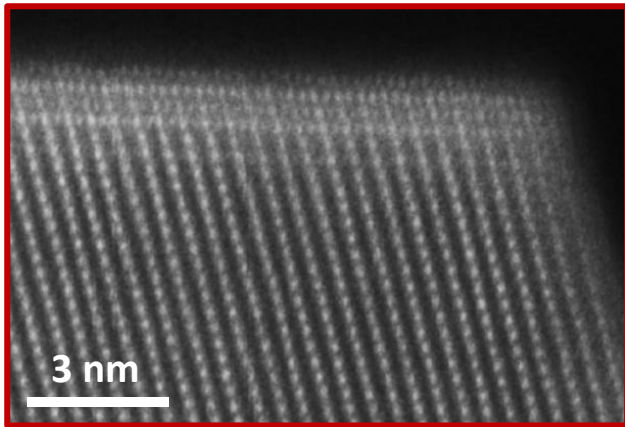


- Selective Ni enrichment on (200) and Co enrichment on (20-2) planes.
- **Pristine oxides have surface-dependent elemental composition.**



# Why surface engineering?

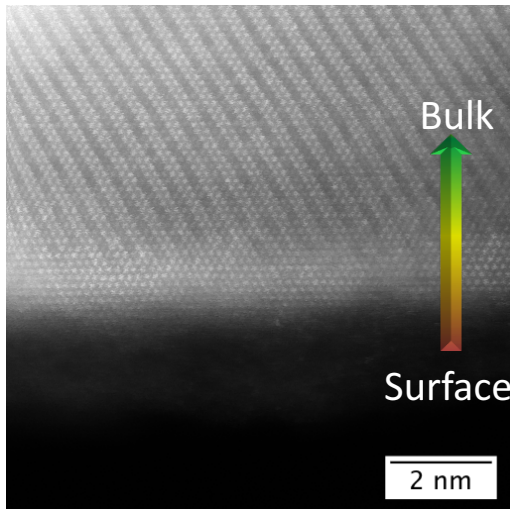
*HAADF STEM imaging (in collaboration with Chongmin Wang, PNNL)*



- Crystal structure transformation observed on pristine surface facets.
- No structural transformation on surface planes aligned with the stacking direction of TM layers.
- **Pristine oxides have surface-dependent crystal structure.**

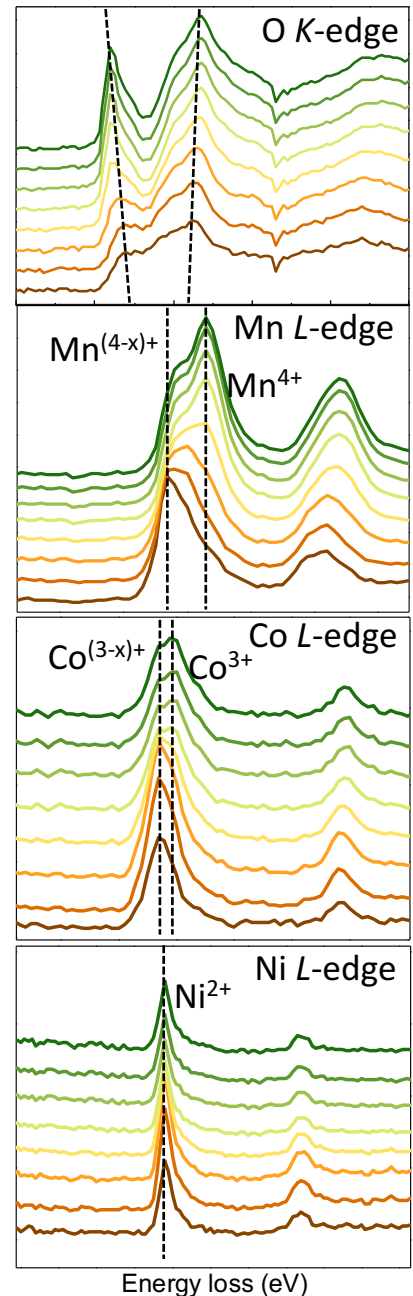
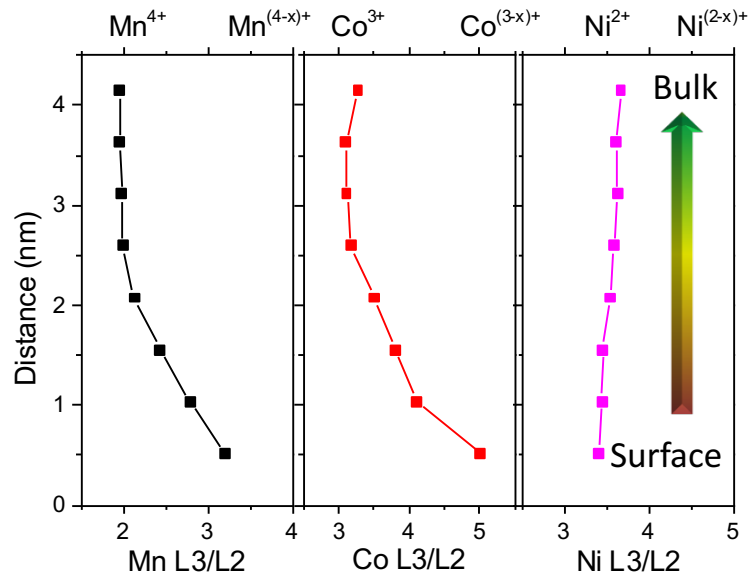
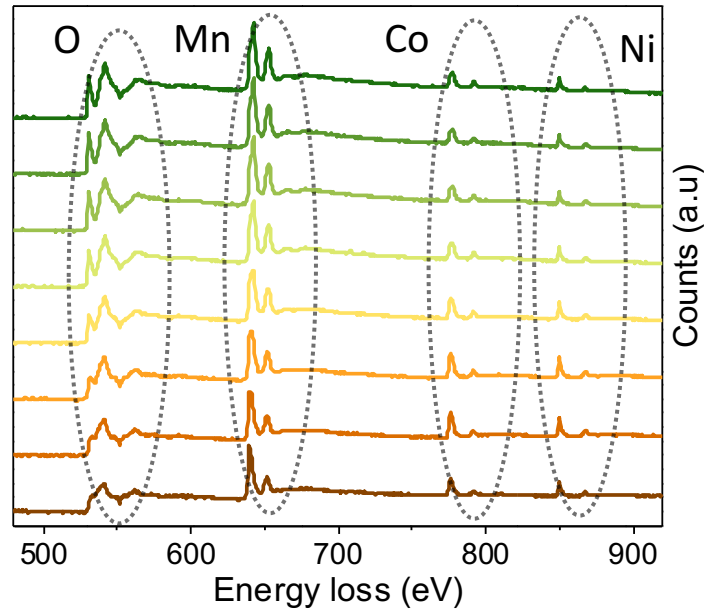
# Why surface engineering?

HAADF STEM imaging and EELS spectroscopy

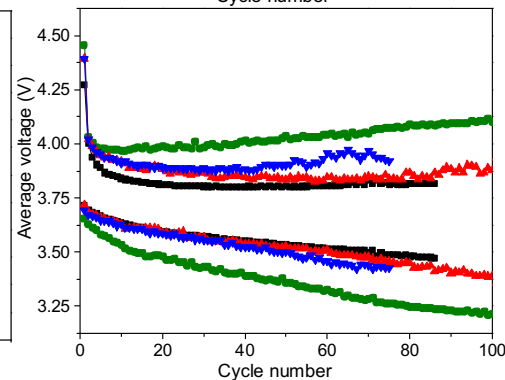
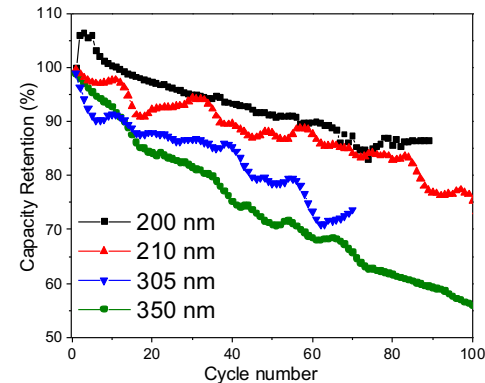
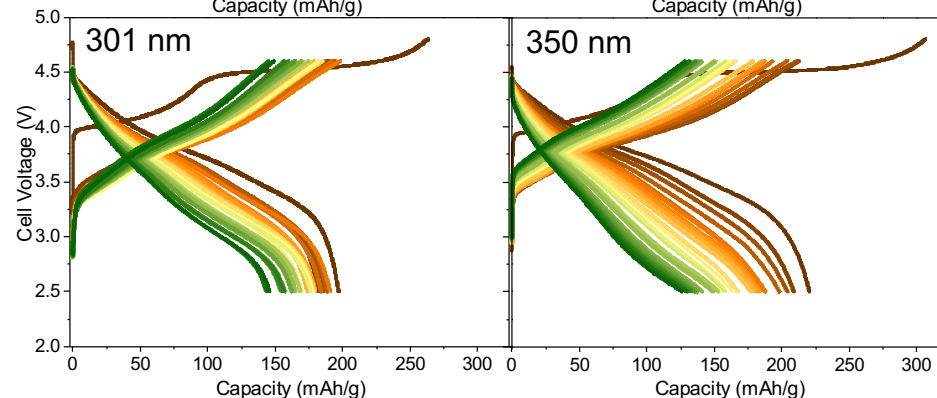
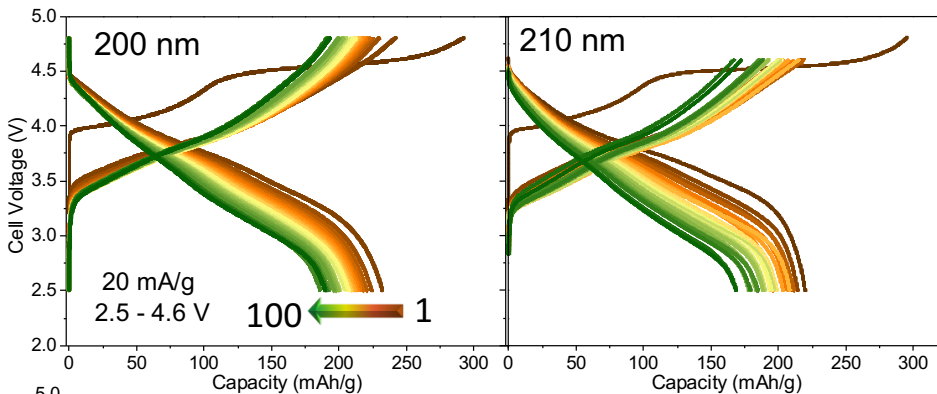
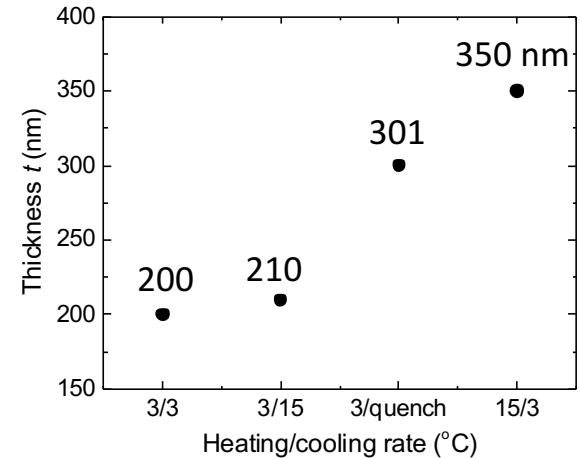
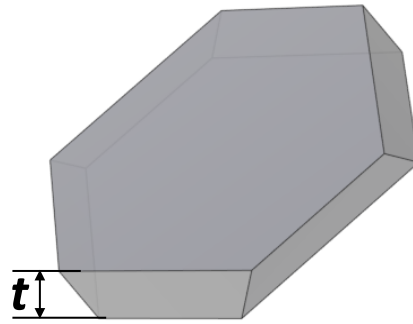
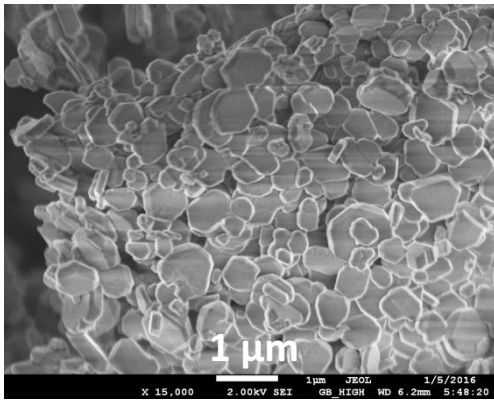


G. Chen et al, *Advanced Energy Materials*, **7**, 1602010 (2017)

- Bulk to surface crystal structural changes accompanied by transition metal reduction and evolution of O environment.
- **Pristine oxides have surface-dependent chemical composition.**
- **Surface engineering important for stabilizing surface oxygen.**



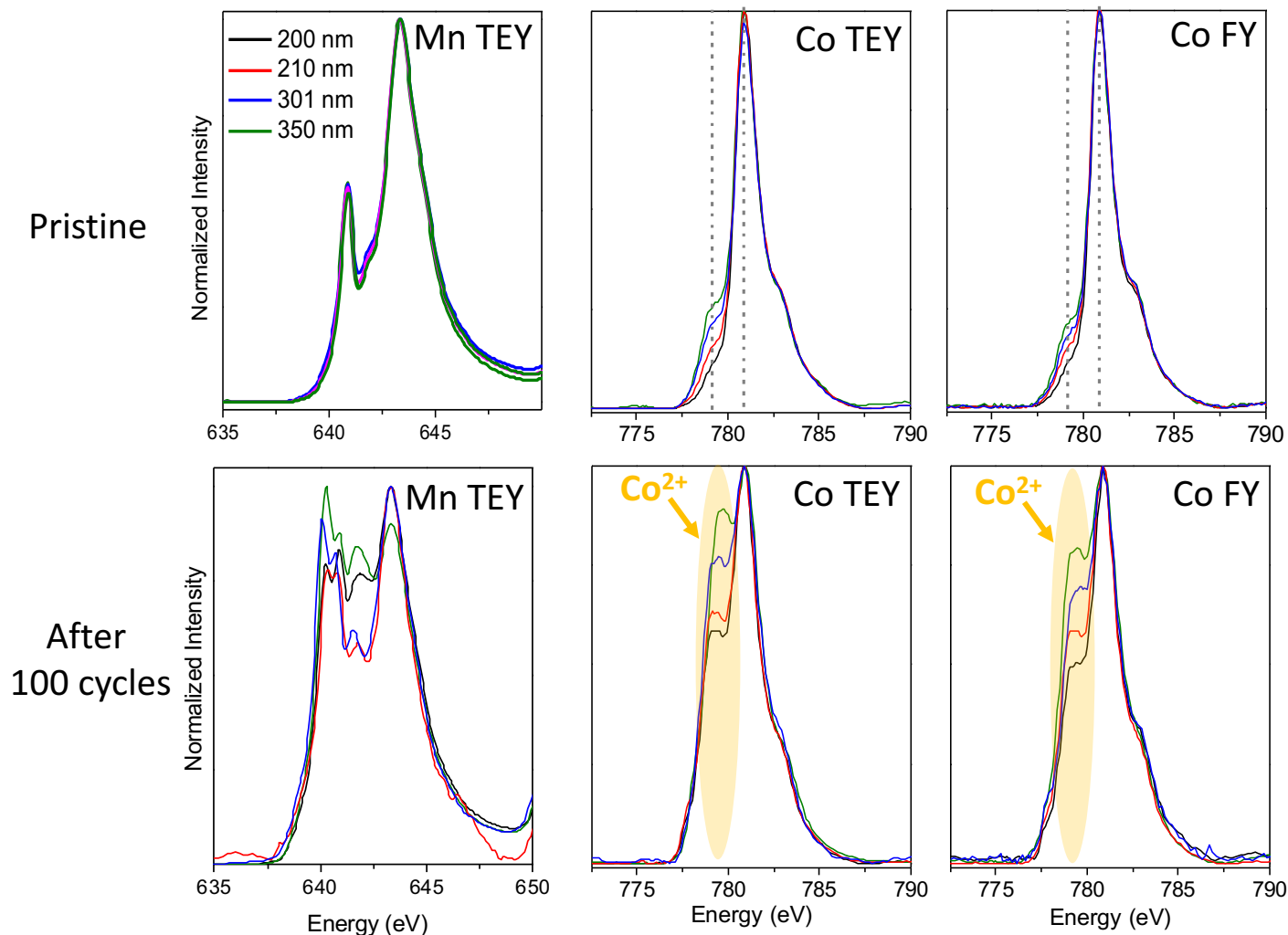
# Strategy – morphology controlled synthesis



- All LMR-NMC141 samples had platelet shape with thickness controlled by heating and/or cooling rate.
- Thickness increase accompanied by increased contribution of facets other than  $(001)_m$ .
- Cycling stability decreases with the increase of platelet thickness.



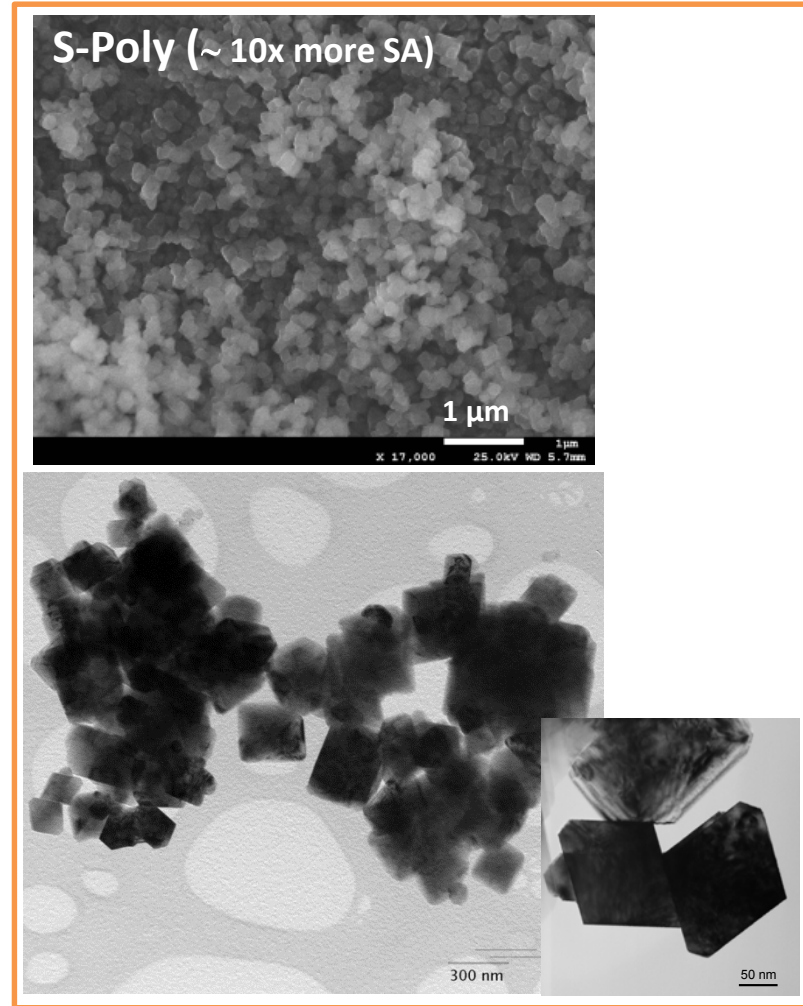
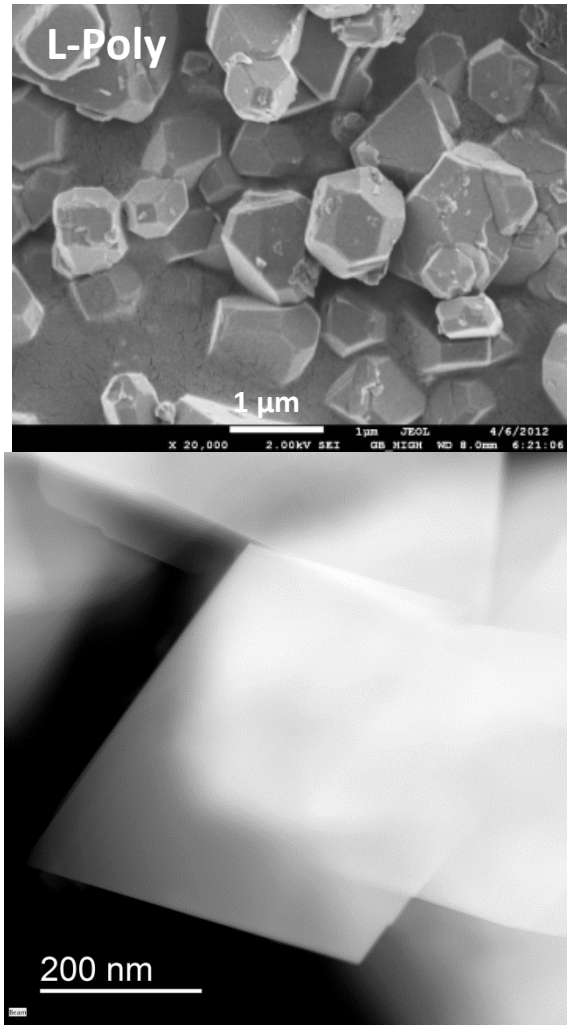
# Strategy – morphology controlled synthesis



*Mn and Co L-edge  
soft XAS  
measurements  
(SSRL beamline 8-2)*

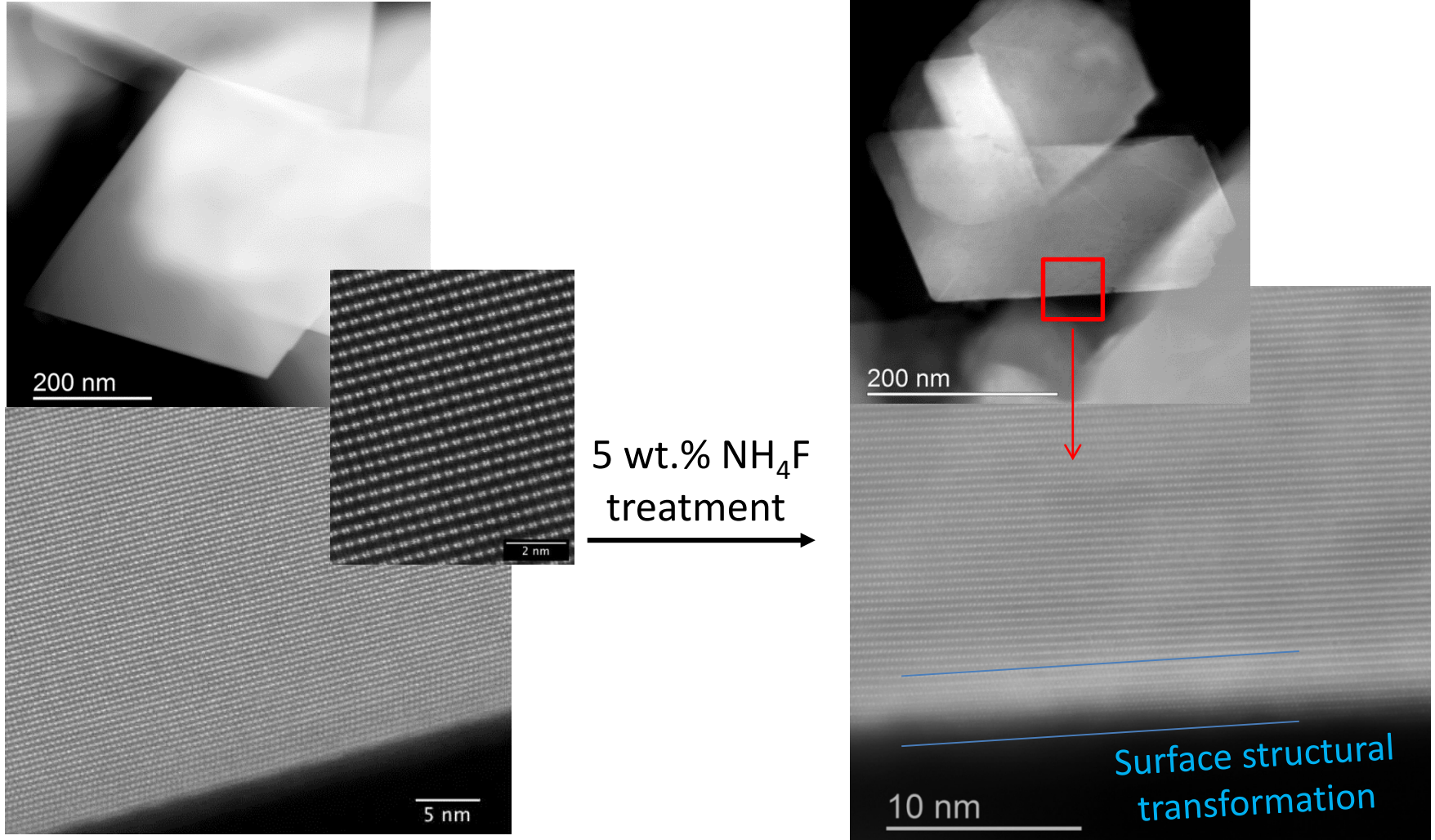
- On pristine, Co reduction increases with the thickness of platelet (facet effect).
- During cycling, both Mn and Co were reduced from surface to bulk but reduction increases with the thickness of platelet – consistent with the trend observed in electrochemical performance.

# Strategy – particle size control and surface coating



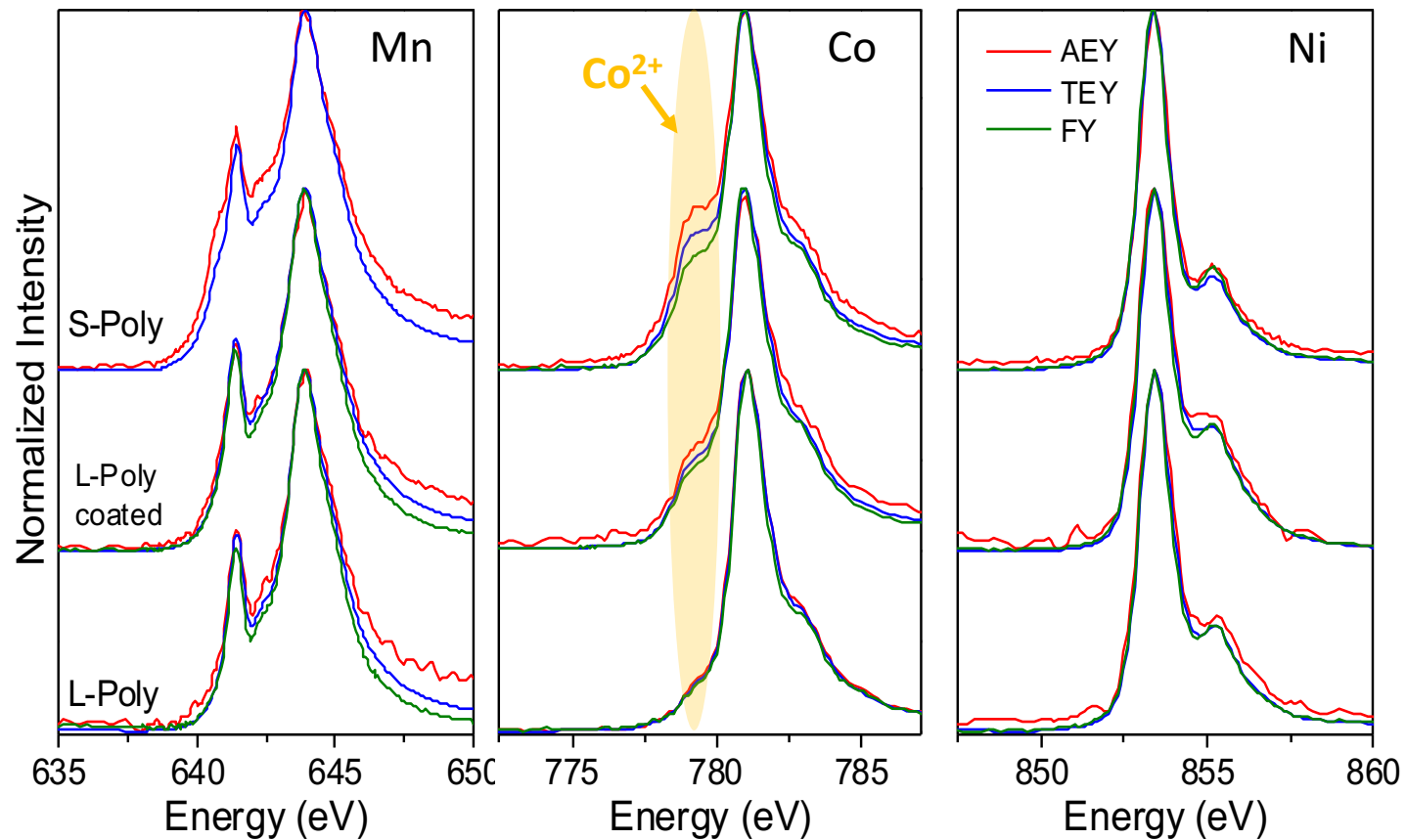
- LMR-NMC141 crystal size varied by adjusting synthesis conditions.

# Coating modifies surface crystal structure



- $\text{NH}_4\text{F}$  coating modifies crystal structure of surface planes aligned with the direction of TM layer stacks (not seen on pristine).

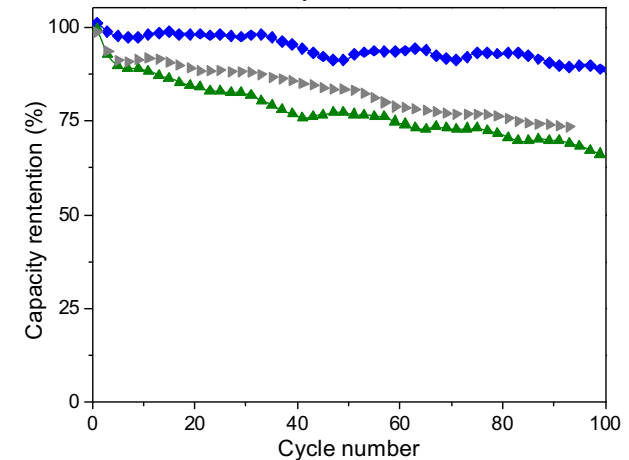
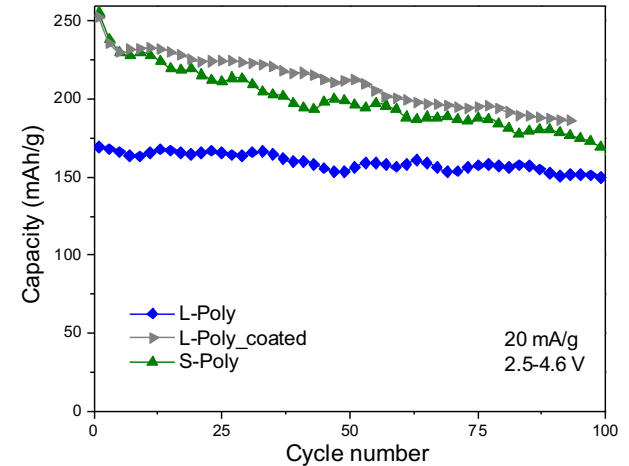
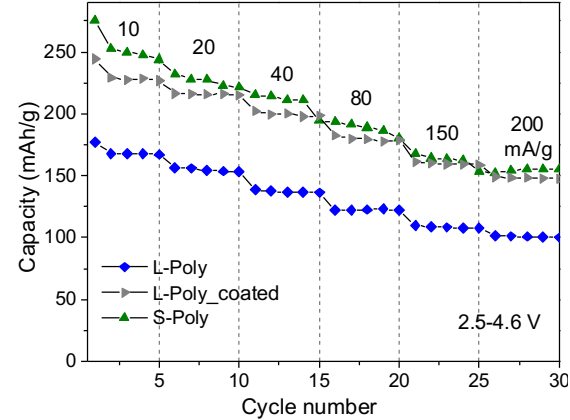
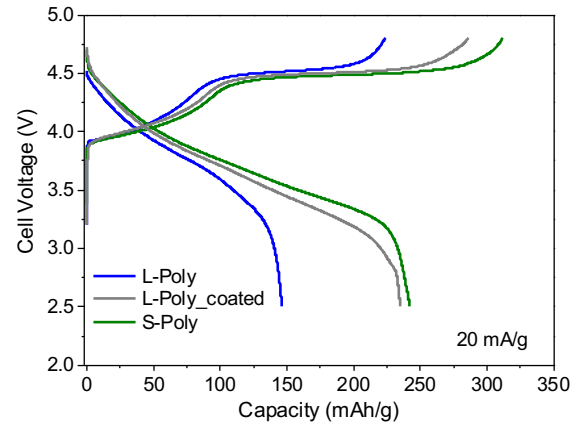
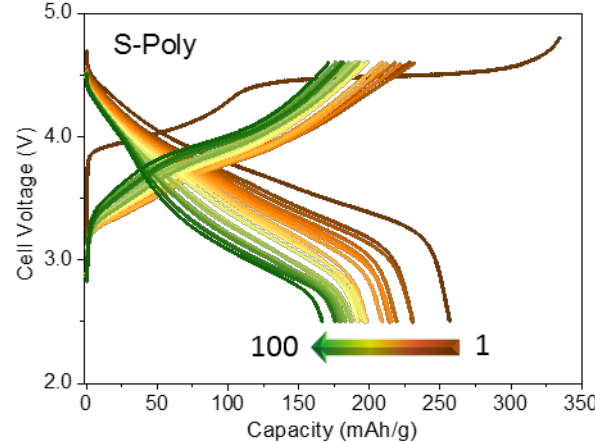
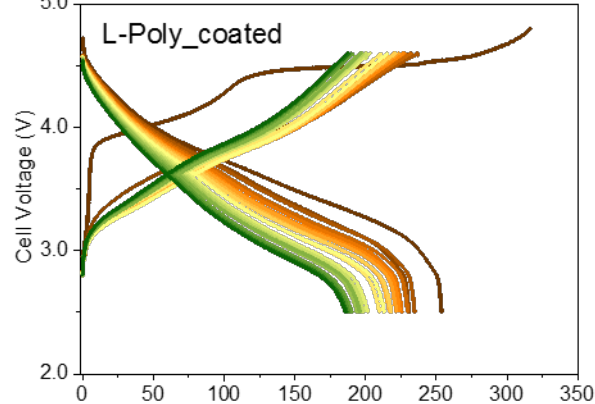
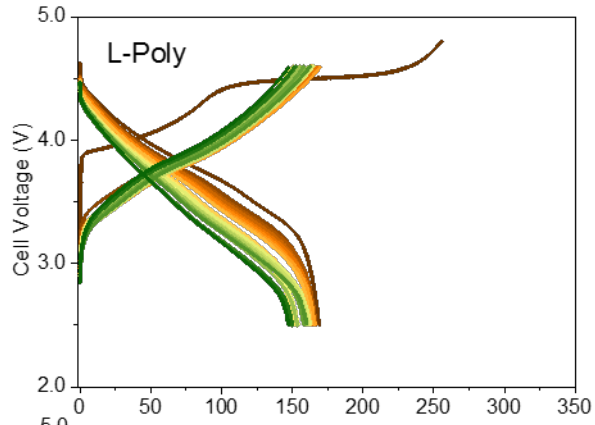
# Coating selectively modifies surface chemical state



- Coating has no effect on the oxidation state of Mn or Ni but enhances Co reduction – similar to particle size reduction.
- Coating decouples chemical modification of transition metals.



# Impact of coating/size reduction



- Particles with less accessible surface can be modified by coating to achieve better activation, utilization and rate capability.
- Impact of coating similar to particle size reduction, enabling the use of large particles.

- Trade-offs between utilization (capacity) and capacity retention (stability) remain.

# Collaborations

- Drs. Marca Doeff (LBNL), Dennis Nordlund and Yijin Liu (SSRL) and APS – synchrotron *in situ* and *ex situ* XRD, XAS and FF-TXM-XANES studies
- Drs. Ethan Crumlin and Jinghua Guo (ALS) – synchrotron XPS, XAS studies
- Dr. Phil Ross (LBNL) and Prof. Simon Mon (Gwangju Institute of Science and Technology, Korea and SPring-8, Japan) – Hard X-ray Photoelectron Spectroscopy
- Prof Bryan McCloskey (UC Berkeley) – DEMS
- Prof. Clare Grey (Cambridge) – NMR studies
- Dr. Ashfia Huq (ORNL) – neutron diffraction
- Dr. Chongmin Wang (PNNL) – STEM/EELS
- Dr. Arun Devaraj (PNNL) – atom probe tomography
- Dr. Jagit Nanda (ORNL) – new cathode material synthesis and characterization



# Remaining Challenges and Barriers

- Activation of anion redox has been shown to increase energy density in Li-excess TM oxide cathodes but fundamental understanding and performance evaluation are needed in order to verify whether O redox can be utilized to develop commercially viable high-energy cathodes.
- Cathode/electrolyte interfacial chemistry is very complex and requires comprehensive understanding using a systematic approach. In order to develop better interface, it is important to determine what reactivity is due to cathode instability and what reactivity is due to electrolyte instability at high voltages.
- Can the trade-offs between cathode capacity (utilization) and capacity retention (stability) be addressed?
- Coating studies can be challenging as there are many variables and the effect likely depends on cathode chemistry/morphology, coating materials and coating techniques used.

# Proposed Future Work

- Further understand cation and anion redox in Li-excess TM oxides and how to best utilize them for developing commercially viable high-energy cathode materials.
  - Investigate electrochemical cycling behavior following 1<sup>st</sup> charge/discharge to evaluate reversibility and kinetics of the anion redox couples.
  - Investigate the impact of having both cation and anion redox activities on cathode performance such as rate capability, structural, cycling and thermal stabilities.
  - Better understand the competing processes of reversible O redox and O<sub>2</sub> release at high voltages.
  - Determine the impact of oxide chemistry/composition, doping, particle morphology and other modifications on O redox activities and their kinetics.
- Obtain comprehensive understanding on the cathode/electrolyte interfacial reactions and processes at high voltages.
- Identify key properties and features hindering stable cycling of Li-TM oxide cathodes at high voltages and develop mitigating approaches to address these issues, particularly regarding oxygen stability on the surface.

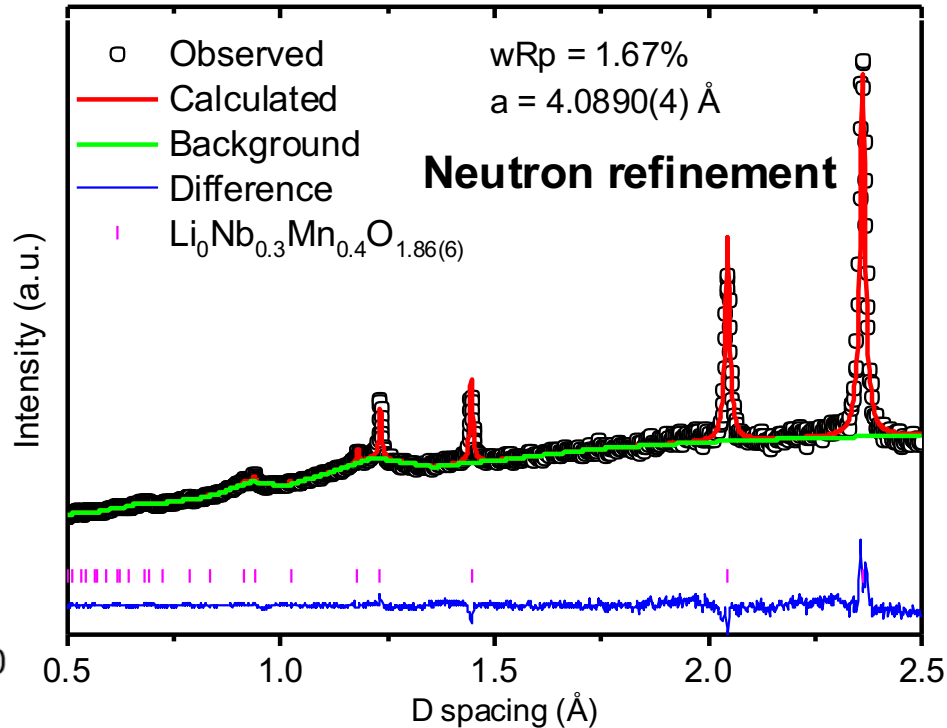
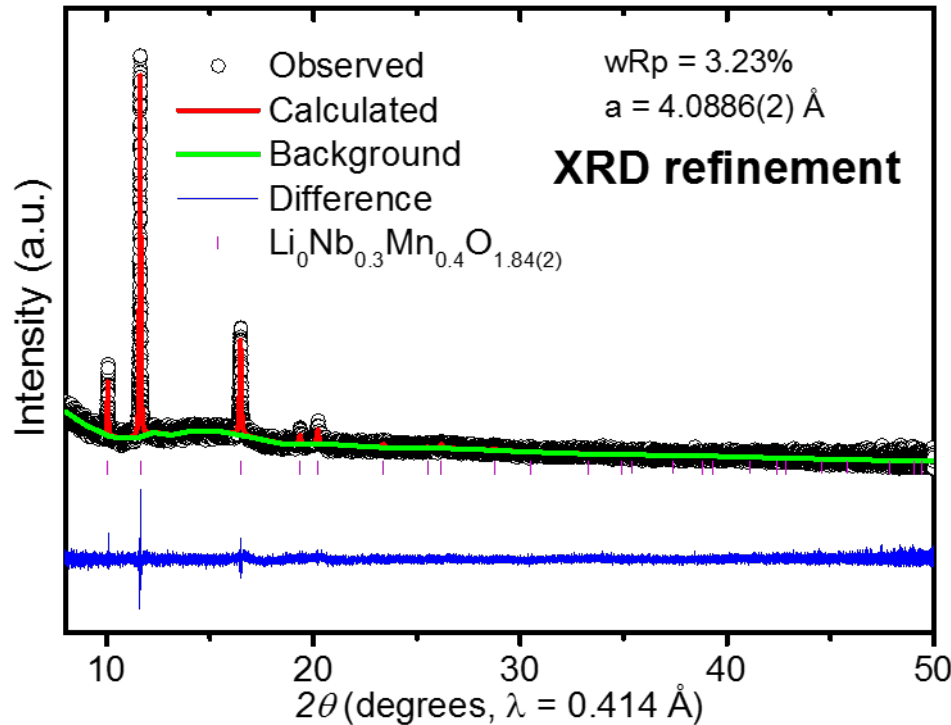
Any proposed future work is subject to change based on funding levels.

# Summary

- Elucidated the charge storage mechanism in a novel high-capacity Li-excess cathode,  $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ 
  - Li extraction occurred in two distinct regions accompanied by Mn redox at low voltage and mixed anion redox at high voltage.
  - Mn oxidation occurred uniformly on entire particles while  $\text{O}^{2-}$  oxidation to  $\text{O}^-$  and  $\text{O}_2$  evolution occurred simultaneously but in separate locations (bulk vs. surface).
  - Linear kinetic behavior of Mn redox and more complex kinetics of O redox observed.
- Evaluated several surface modification strategies in improving high-voltage cycling stability of LMR cathodes
  - Cathode cycling stability closely related to chemical composition on the surface.
  - Surface facet engineering important for improving cycling performance. Correlations between morphology and synthesis conditions exist.
  - Coating can modify surface chemical composition and crystal structure.
  - Surface coating improves utilization/kinetics and may enable the use of large primary particles.

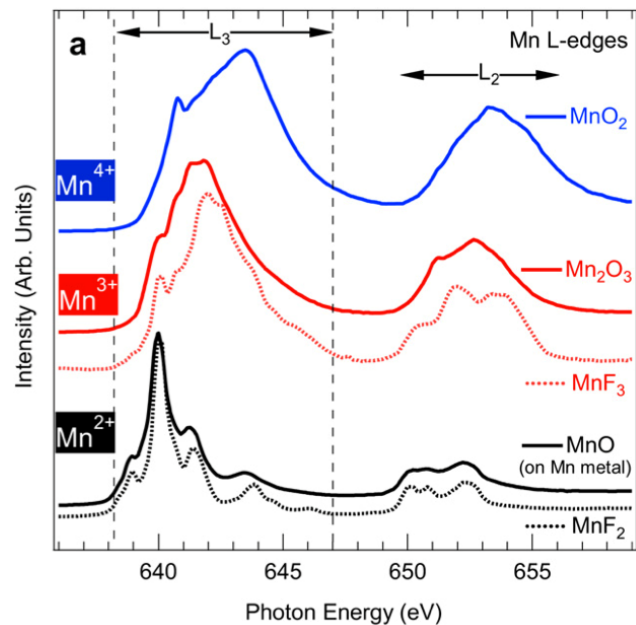
# **Technical Back-Up Slides**

# $\text{Li}_x\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ – structural refinement

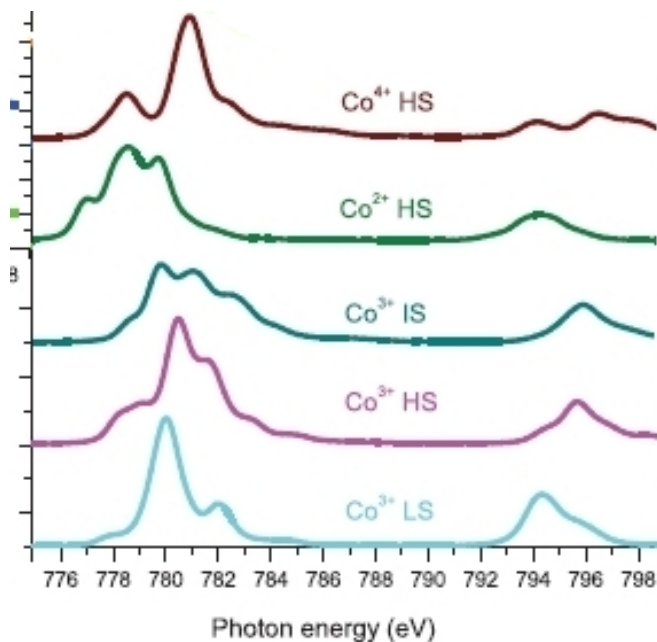


- Structural data was obtained through combined refinement of synchrotron XRD (APS) and neutron (ORNL) patterns of the samples.
- Refined oxygen occupancy is 0.92(1) or 8% of oxide ion vacancy in fully delithiated sample, corresponding to a formula of  $\text{Li}_0\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_{1.84(2)}$ .

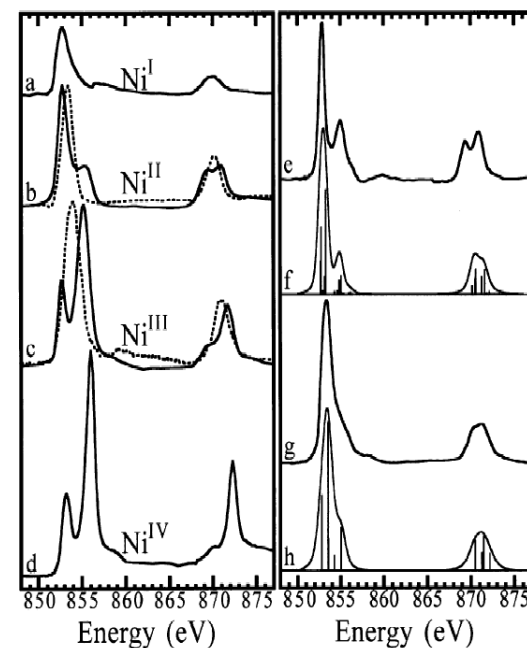
# Standard soft XAS spectra for transition metals



*Journal of Electron Spectroscopy and Related Phenomena* 190, 64–74 (2013)



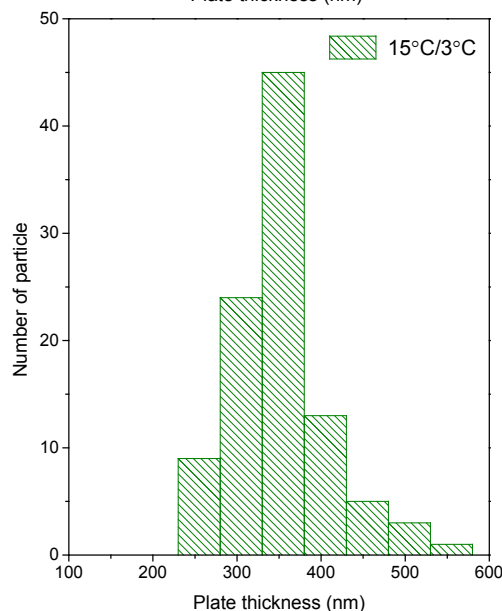
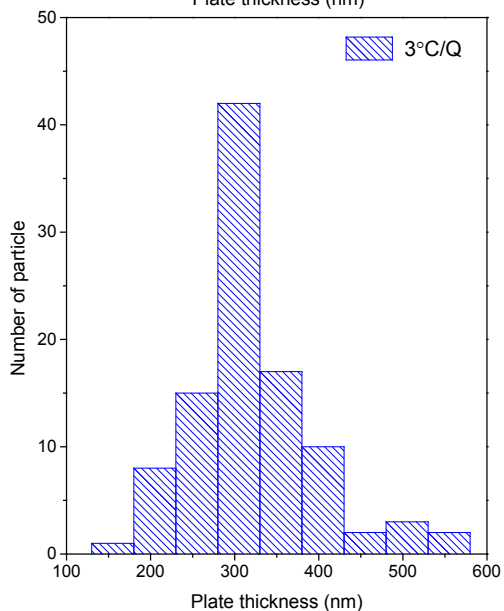
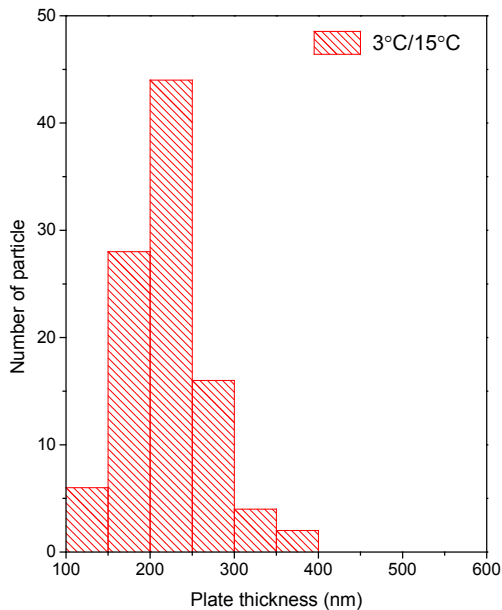
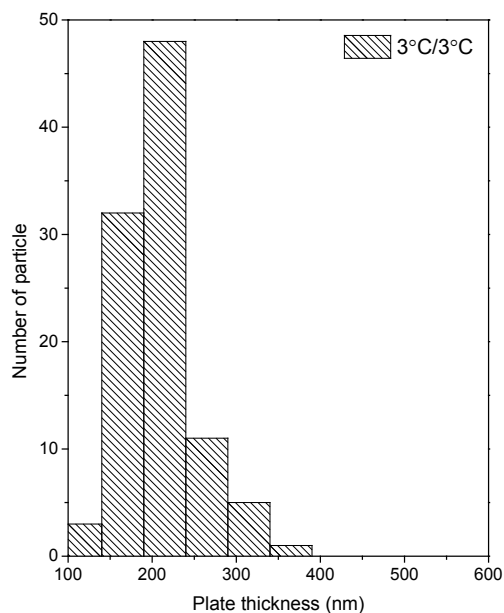
*Physical Review B* 84, 014436 (2011)



*Journal of Electron Spectroscopy and Related Phenomena* 114–116, 855–863 (2001)



# Thickness distribution of the LMR-NMC141 platelets



Sample	Mean (nm)	Median (nm)
3°C/3°C	203.79	200
3°C/15°C	215.51	210
3°C/Q	303.41	301
15°C/3°C	352	350

- Thickness of the platelets was determined by surveying a large number of the crystals under SEM.